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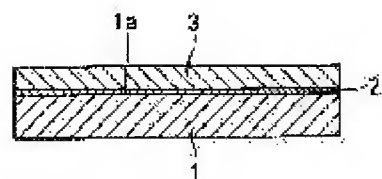
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(54) COATING METHOD FOR TITANIUM METAL WITH VITREOUS CARBON

(57)Abstract:

PROBLEM TO BE SOLVED: To form homogeneous vitreous carbon film with a high amorphousness on the surface of titanium metal and to efficiently form this vitreous coating on the surface of the titanium metal as thin film.

SOLUTION: The surface of titanium metal 1 is polished by buffing using, as abrasives, emery paper, alumina and a suspension of chromium oxide to form a mirror face 1a, a dense and firm titanium oxide coating layer 2 on the mirror face 1a, and the surface of the titanium oxide coating 2 is subjected to plasma heat treatment in an atmosphere of 0.1 to 30 Torr×400 to 1100°C contg. gaseous hydrocarbon such as methane, ethane, propane or the like to form vitreous carbon coating 3 on the surface of the titanium metal.



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CLAIMS

[Claim(s)]

[Claim 1]Form a tunic of titanium oxide in the titanium metal surface precisely, and the surface of a tunic of this titanium oxide 0.1 - 30torr of hydrocarbon system gas content, A coating method of glassy carbon to a titanium metal which consists of covering glassy carbon by carrying out plasma heat treatment within 400-1100 ** atmosphere.

[Claim 2]Grind the titanium metal surface, form a mirror plane, and a tunic of titanium oxide is formed on this mirror plane, A coating method of glassy carbon to a titanium metal which consists of covering glassy carbon by carrying out plasma heat treatment of the surface of a tunic of this titanium oxide within 0.1 - 30torr of hydrocarbon system gas content, and 400-1100 ** atmosphere.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the coating method of the glassy carbon to a titanium metal.

[0002]

[Description of the Prior Art]Since a titanium metal excels [heat resistance] in specific strength highly and generally forms an oxide layer in the surface in the air, having the character excellent in corrosion resistance is known. Unalloyed titanium can build all the metal especially copper, tin, iron, aluminum, vanadium, chromium, cobalt, molybdenum, nickel, etc. and an alloy, and can improve various the processability and mechanical strengths.

[0003]The titanium metal which consists of such unalloyed titanium or a titanium alloy is activity metal, and the surface oxidizes promptly in the air. The tunic which consists of titanium oxide formed in the surface at this time shows the corrosion resistance excellent also in corrosive environment, and is also called the passivation film by the protective action of that tunic.

[0004]After the artificers of this application did cleaning treatment of the titanium metal surface by earlier application and removed the oxide film, they did carburizing treatment, and they reduced surface friction / wear coefficient, the raw material useful as conclusion material, such as a sliding material and a bolt nut, was developed, and the process was indicated to JP,7-90542,A.

[0005]By the way, glassy carbon is carbon (difficulty graphitization nature carbon) which graphite structure does not progress even if the several nanometers hex-steel side which is the basic structure of graphite system material is gathered without directivity and it heat-treats it to the elevated temperature near 3000 **, but has a near structure amorphously. The high glassy carbon of amorphous nature has the outstanding characteristics with high value for industrial Agari, such as corrosion resistance, abrasion resistance, lubricity (low friction coefficient), a mold-release characteristic, and gas impermeability.

[0006]In order to manufacture the Plastic solid which consists of such glassy carbon, After fabricating charges of a thermosetting resin material, such as phenol, to required shape and

polymerizing and heat-hardening this, it was machined, and carbonized by heating a Plastic solid on strict temperature control conditions, and carrying out temperature up very gradually further, and the glassy carbon Plastic solid had been acquired.

[0007]

[Problem(s) to be Solved by the Invention]In order to apply the process of the above-mentioned conventional glassy carbon and to form a vitrified carbon film on the surface of a metal body, the charge of a thermosetting resin material is covered on the surface of a Plastic solid, and how to heat this under temperature control conditions for a long time can be considered.

[0008]However, in such a method, the layer with which the metal and glassy carbon of the ground mingled is formed, or the carbide of a substrate metal is formed, A homogeneous vitrified carbon film cannot be formed on the surface of a titanium metal, and a vitrified carbon film cannot be efficiently formed in a molded body surface at a thin film, either.

[0009]Then, the technical problem of this invention is solving the above-mentioned problem, and forming the homogeneous high vitrified carbon film of amorphous nature on the surface of a titanium metal, and forming such a vitrified carbon film in a thin film efficiently on the surface of a titanium metal.

[0010]It is providing the coating method of the glassy carbon with sufficient working efficiency to a titanium metal production form, and providing the surface treatment method which corrosion resistance, abrasion resistance, lubricity (low friction coefficient), a mold-release characteristic, gas impermeability, and biocompatibility are high, and can raise the utility value on the industry of a titanium metal.

[0011]

[Means for Solving the Problem]In [in order to solve the above-mentioned technical problem] this invention, Form a tunic of titanium oxide in the titanium metal surface precisely, and the surface of a tunic of this titanium oxide 0.1 - 30torr of hydrocarbon system gas content, It was considered as a coating method of glassy carbon to a titanium metal which covers glassy carbon by carrying out plasma heat treatment within 400-1100 ** atmosphere.

[0012]Or grind the titanium metal surface, form a mirror plane, and a tunic of titanium oxide is formed on this mirror plane, It was considered as a coating method of glassy carbon to a titanium metal which covers glassy carbon by carrying out plasma heat treatment of the surface of a tunic of this titanium oxide within 0.1 - 30torr of hydrocarbon system gas content, and 400-1100 ** atmosphere.

[0013]As for a formation method of a mirror plane over the above-mentioned titanium metal surface, it is preferred that it is buffing which used emery paper, alumina suspension, and chrome oxide suspension as abrasive soap.

[0014]In a coating method of glassy carbon to a titanium metal of this invention, a tunic of very precise and firm titanium oxide is formed in the titanium metal surface. As said titanium oxide, it is titanium oxide. (II) (TiO), titanium oxide (III) (Ti₂O₃), titanium(IV) oxide (TiO₂), etc. are mentioned.

[0015]As a formation method with a suitable precise tunic which consists of titanium oxide, The

titanium metal surface is ground, it is performing polishing work by buffing preferably, even if it is very precise and sees according to a smooth side, i.e., a naked eye, by this, an optical reflector (mirror plane) which that it is a mirror plane can distinguish is formed, and a titanium oxide film of protection nature is simultaneously formed on a mirror plane. If it oxidizes in ordinary temperature, heated air, or a compulsory oxidizing atmosphere even if it does not carry out mirror finish, a tunic of titanium oxide which uses titanium(IV) oxide etc. as the main ingredients can be formed very precisely.

[0016]thus, a tunic of titanium oxide formed precisely -- the inside of said predetermined atmosphere -- plasma **** of a predetermined condition, and penetration (carburization) into a titanium metal of a carbon ion activated on the occasion is prevented or controlled. Therefore, high carbon of amorphous nature accumulates on the surface of a tunic of titanium oxide, and a vitrified carbon film of a thin film is covered with plasma heat treatment of a predetermined condition by the titanium metal surface by high homogeneity of amorphous nature via a tunic of titanium oxide.

[0017]

[Embodiment of the Invention]The titanium metals used for this invention may be any of the intermetallic compound of unalloyed titanium, a titanium alloy or titanium, and other metal.

[0018]By forming a mirror plane in the surface of the above-mentioned titanium metal, polish as used in the field of this invention is performed in order to form a very precise and firm oxide layer. The grinding method in that case may be a grinding method of the common knowledge adopted when carrying out mirror finish of the metal, and buff (aircraft cloth) polish, other mechanical polishing, and chemical polish can be used for it. The desirable result has been obtained also when buffing which used emery paper and alumina suspension, and chrome oxide suspension as abrasive soap is adopted as a grinding method.

[0019]Before carrying out plasma heat treatment of the above mentioned titanium metal, a mirror plane is formed by above-mentioned grinding treatment, but it is desirable to perform washing processing which immersed the surface in the organic solvent just before carrying out plasma heat treatment, or uses an ultrasonic wave.

[0020]In order to perform plasma heat treatment, form the processing chamber surrounded with thermal insulation, such as a graphite fiber, in a heating furnace, heat the inside of this processing chamber with the heating element which consists of rod graphite, and. Connect the anode of direct-current glow discharge to the upper part in a processing chamber, and the negative pole is connected to the mounting base of a processing article, The publicly known carburizing treatment device (made by a JEOL industrial company) introduced while installing a gas manifold in the key point in a processing chamber and distributing suitably process gas or the gas for cleaning, such as hydrocarbon, nitrogen, argon, and hydrogen, can be used.

[0021]That is, the following operations can perform plasma heat treatment of this invention. First, after inserting in and exhausting a titanium metal etc. to a processing chamber, it heats even at 400-1100 ** with a heater, the gas for cleaning which consists of inactive gas, such as argon and nitrogen, or hydrogen gas for dilution is introduced, the direct current voltage of 200-1500V is impressed, and it holds for 10 to 30 minutes.

[0022]although the introduced gas is plasma-ized at this time -- the potential in plasma -- from the anode up to [the great portion of] the negative pole -- about -- it is Mr. one and potential falls rapidly near the negative pole. For this reason, it is accelerated by a cathode drop, and hydrogen ion H^+ in plasma and argon ion Ar^+ collide with the titanium metal surface, bound a surface affix off, and clean the titanium metal surface. However, as mentioned above, since the oxide layer on a mirror plane has adhered very precisely and firmly, even if it receives an operation of sputtering, such as argon and hydrogen, it remains.

[0023]Next, if hydrocarbon system gas, such as methane and propane, is introduced in the range of 0.1 - 30torr, into plasma gas, ionized activation carbon C^+ occurs, and this will adhere to the titanium metal surface and will accumulate.

[0024]The hydrocarbon system gas used in this invention may be a general term for the gas which consists only of carbon and hydrogen, and chain hydrocarbon may also be which compound of cyclic hydrocarbon. The hydrocarbon of methane series etc. which are shown by H_{2n} of general formula $C_n H_{2n+2}$ as an example of representation of chain hydrocarbon. The hydrocarbon of ethylene series (general formula $C_n H_{2n}$) and the hydrocarbon of acetylene series (general formula $C_n H_{2n-2}$) are mentioned, and it may be straight chain shape or may have a side chain. In particular, at ordinary temperature, when using it, since vaporization equipment is unnecessary, gaseous methane, ethane, propane, and butane can be said to be desirable. As cyclic hydrocarbon, it may be any of aromatic compounds or an alicyclic compound, and benzene (C_6H_6) is mentioned as an example of representation of aromatic compounds.

[0025]Here, the pressure of the hydrocarbon system gas on the conditions of the above mentioned plasma heat treatment is 0.1 - 30torr. It is required in order to mainly form a glassy carbon (glass-like carbon) film in the titanium metal surface, and the pressure of such hydrocarbon system gas has few carbon contents of a membrane formation layer, and its low pressure of less than 0.1 torr is not enough as membrane formation. In the high voltage exceeding 30torr, it is because it becomes less practical. From such a tendency, the pressure of more desirable hydrocarbon system gas is 0.1 - 20torr.

[0026]The ambient temperature of the plasma heat treatment in this invention is 400-1100 **. Because, in the low temperature below 400 **, the adhesion of the glassy carbon on the surface of a titanium metal becomes low. In the elevated temperature over 1100 **, it is because the treatment temperature beyond this is not practical also in order to secure the strength property of titanium.

[0027]

[Example]The surface of a 3-mm-thick plate-like beta titanium alloy (Ti-15V-3aluminum-3Cr-3Sn) at length and 30 mm wide After 1200 emery polish, Buff (buff) which uses alumina ($aluminum_2O_3$) suspension as abrasive soap Mirror finish was carried out by polish, it cleaned ultrasonically in acetone, and plasma heat treatment was performed on the following device and conditions.

[0028]Namely, have the processing chamber surrounded with thermal insulation, such as a graphite fiber, in the heating furnace, and heat the inside of this processing chamber with the heating element which consists of rod graphite, and. The publicly known carburizing treatment device (made by a JEOL industrial company) which connects the anode of direct-current glow discharge to the upper part in a processing chamber, connects the negative pole to the mounting base of a processing article, and installs a gas manifold in the key point in a processing chamber, and introduced process gas, such as hydrocarbon, nitrogen, argon, and hydrogen, suitably was used.

[0029]And as plasma-heat-treatment conditions, gas composition was made into propane 100%, and as treatment temperature of 800 **, nitrogen gas was pressed fit in the processing chamber after processing, and it cooled even in ordinary temperature for gas pressure 1Torr, and processing time 90 minutes.

[0030]The ingredient of the film which performed the ESCA broad spectrum by the semiquantitative analysis by ** X-ray microanalyser (EPMA), ** Raman spectroscopic analysis, and **X linear-light electronic spectroscopic analysis, and was formed in the surface of the metal piece of an example about the metal piece of the example which processed more than, and its crystal structure were investigated.

[0031]First, it was as the chemical entity near the surface gloss film (% of the weight) being the following about the result of the above-mentioned **.

Ti: 54%, C:28%, V:13%, Sn:3%, aluminum: It was as the chemical entity of the substrate of a beta titanium alloy being the following O:0.4% again 1%.

Ti: 65%, C:2%, V:22%, Sn:5%, aluminum : as a chemical entity near the surface gloss film from the Si:2% above-mentioned result 3% and O:1%, It turns out that only original carbon and oxygen other than an ingredient of a substrate of a beta titanium alloy are detected, and the carbide which is a compound of a titanium alloy and carbon is not generating.

[0032]About ** Raman spectroscopic analysis, the Raman spectrum was measured using the micro Raman spectral device, and the structure of carbon was investigated. The measuring condition made excitation light Ar^+ laser, 514.5 nm, 40 mW, and microscope magnification 50 times, and irradiation time 10 seconds using the Lamaism scope type micro Raman spectral device of the product [measuring device] made by Renishaw.

[0033]From the result of ** shown in drawing 1, the peak of the crystalline carbon origin of a Raman spectrum is near 1580-cm^{-1} , And since the peak originating in amorphous carbon is near 1350-cm^{-1} and such a peak is in agreement with the classic example of glassy carbon, it can check that the film formed in the surface of the metal piece of an example is glassy carbon.

[0034]The peak of the ESCA broad spectrum by X linear-light electronic spectroscopic analysis is near 532 eV which shows the existence of near 285 eV and oxygen which shows existence of carbon, and only carbon and oxygen were detected from the result of ** shown in drawing 2. These things show that the coated layer 2 of titanium oxide is formed on the mirror plane 1a of the titanium metal 1 as the film of glassy carbon homogeneous in the surface of the metal

piece of an example shows drawing 3, and the vitrified carbon film 3 of equivalent thickness is formed on it.

[0035]

[Effect of the Invention]In this invention, as explained above, the tunic of titanium oxide was precisely formed on the mirror plane of a titanium metal, and plasma heat treatment of the surface of the tunic of this titanium oxide was carried out according to the predetermined condition.

Therefore, the homogeneous high vitrified carbon film of amorphous nature is formed on the surface of a titanium metal, and such a vitrified carbon film can be efficiently formed in a thin film on the surface of a titanium metal.

[0036]The coating method of the glassy carbon with sufficient working efficiency to a titanium metal production form can be provided, corrosion resistance, abrasion resistance, lubricity (low friction coefficient), a mold-release characteristic, gas impermeability, and biocompatibility are high, and there is also an advantage used as the surface treatment method which can raise the utility value on the industry of a titanium metal.

[Translation done.]